

## Supporting Information

### Kinetics of chlorination of benzophenone-3 in the presence of bromide and ammonia

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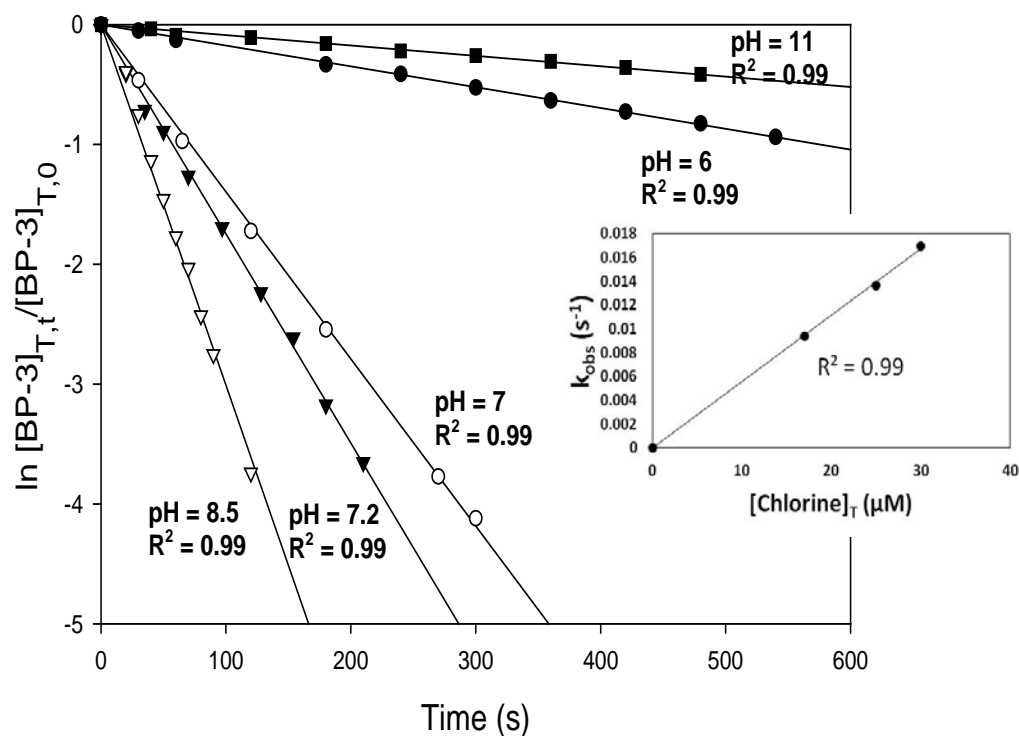
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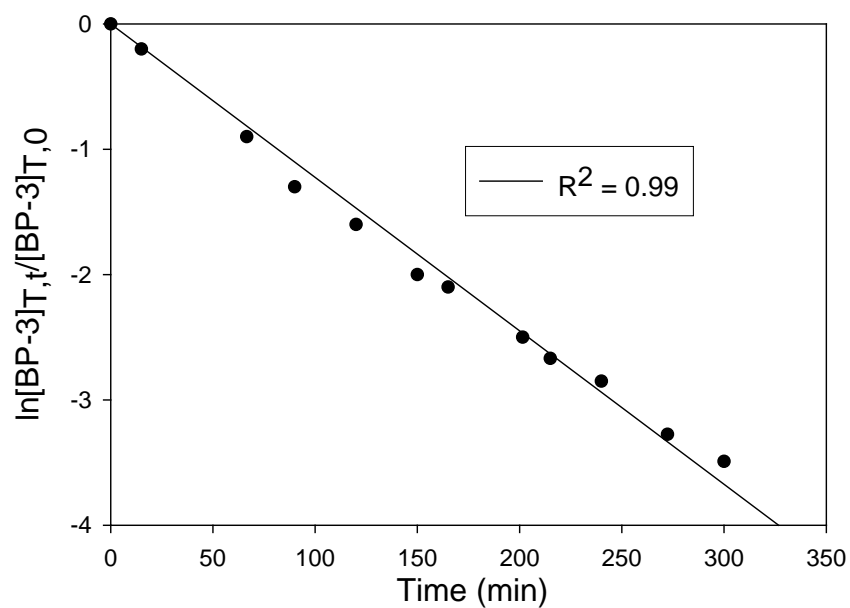
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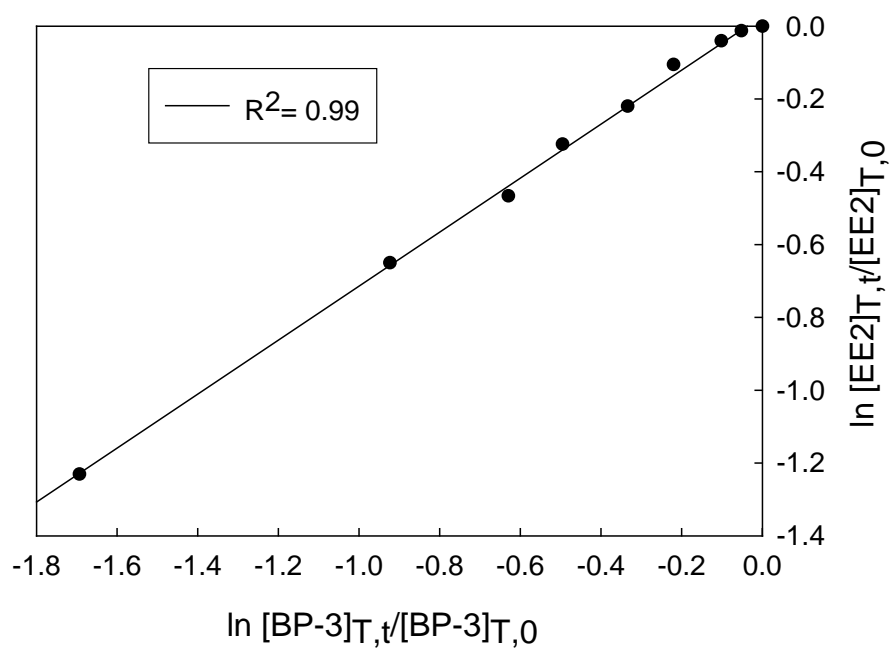
## Kinetic Study: Chlorination, Chloramination and Bromination of BP-3



**Figure S1.** Example pseudo first-order kinetic plots for BP-3 chlorination at different pH values and  $20 \pm 2^\circ\text{C}$  ( $[\text{BP-3}]_{T,0} = 1.5 (\pm 0.3) \mu\text{M}$ ,  $[\text{Chlorine}]_{T,0} = 30 (\pm 5) \mu\text{M}$ );  
insert: BP-3 chlorination at pH 7,  $20 \pm 2^\circ\text{C}$  and various  $[\text{Chlorine}]_{T,0}$



**Figure S2.** Chloramination of BP-3 at pH 8.5,  $T = 20 (\pm 2)^\circ\text{C}$   
 $([\text{BP-3}]_{T,0} = 1 \mu\text{M} ; [\text{NH}_2\text{Cl}] = 1.7 \text{ mM})$



**Figure S3.** Example kinetic study of the bromination of BP-3 in the presence of EE2 at pH 7  
 $([\text{BP-3}]_{T,0} = [\text{EE2}]_{T,0} = 3 \mu\text{M} ; [\text{Bromine}]_{T,0} = 0\text{-}15 \mu\text{M})$

### **Comparison with other phenolic compounds: Hammett type correlations**

Figure S4a and S4c represent the  $\log k_2$  as a function of  $\sum\sigma_{(o,m,p)}$  by considering data from various studies <sup>(1-8)</sup> according to Heeb et al. (2014) and Duirk et al. (2013) <sup>(9,10)</sup>. In these figures, the Hammett constants were from Hansch et al. (1991) <sup>(11)</sup>, and  $\sum\sigma_{(o,m,p)}$  was calculated for every molecule by considering phenol as the reference compound (i.e.  $\sum\sigma_{(o,m,p)}=0$ ) <sup>(9,10)</sup>. For both oxidants (chlorine and bromine), a negative Hammett slope was noted, consistent with the electrophilic substitution mechanism. In the case of chlorination, different Hammett relationships were observed between monohydroxy and metadihydroxybenzenes. For the same  $\sum\sigma_{(o,m,p)}$  values, rate constants of metadihydroxybenzenes were more than one order of magnitude higher than those of monohydroxybenzenes. This higher sensitivity of metadihydroxybenzenes towards HOCl substitution could be explained by the meta electron-donor substituent which directs chlorine substitution at similar sites to the phenolic function (i.e. in ortho and/or para position to the phenolic function) <sup>(2,12)</sup>. Surprisingly, the calculation for benzophenone-3 (Figure S4a), i.e. a monosubstituted phenol, showed a better correlation with metadihydroxybenzenes. This could be due to the presence of the electron-donor methoxy substituent  $-\text{OCH}_3$  in meta position to the phenolic function, similarly to metadihydroxybenzenes. Only monohydroxybenzene data are represented in Figure S4c in the case of bromination. However, a similar behavior was observed for BP-3, with a higher reactivity of the latter compared to the Hammett relationship obtained for monohydroxybenzenes <sup>(1,3,5-8)</sup>.

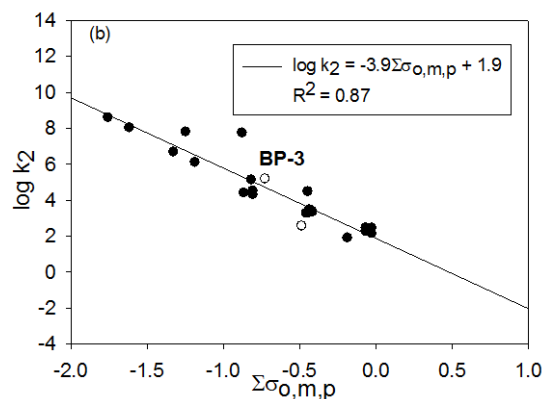
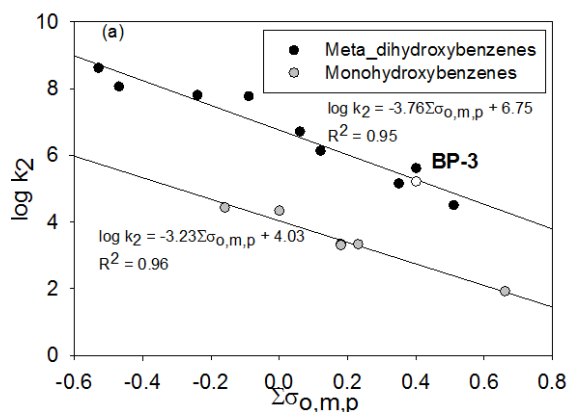
A corrected Hammett-type correlation was previously suggested for phenol chlorination by Deborde and von Gunten <sup>(12)</sup>. In this latter correlation, benzene was used as a reference compound and Hammett substituent constants were calculated by considering attack on the most probable site(s) of chlorine attack (i.e. unsubstituted ortho or/and para position(s) to the phenolic function) from the Hammett constants given by Perrin et al. (1981) <sup>(13)</sup>. This

correlation is shown in Figure S4b for monohydroxy and metadihydroxybenzene chlorination<sup>(26,29,30)</sup>. Similarly, in the present study, this correlation was applied for bromination of phenols using literature data (Figure S4d). Under these conditions, for a given compound, if all attack sites were occupied, the non-halogenated site in ortho or para position to the phenol function was considered as the reference site. For  $\sum\sigma_{(o,m,p)}$  calculations, the  $\sigma_m$  value was used for the substituent present on the reference site. The results show a good linear correlation ( $R^2 = 0.87$ ) with no difference between mono and metadihydroxybenzenes for both chlorination and bromination by using this corrected Hammett relationship. Moreover, a good agreement was obtained between BP-3 and the corrected Hammett-type correlations for both studied oxidants. In light of these results, a similar reaction mechanism based on electrophile substitution on the ortho and/or para sites to the phenol function would be expected during chlorination or bromination of BP-3. The formation of mono, di and trihalogenated derivatives is therefore expected<sup>(14,15)</sup>.

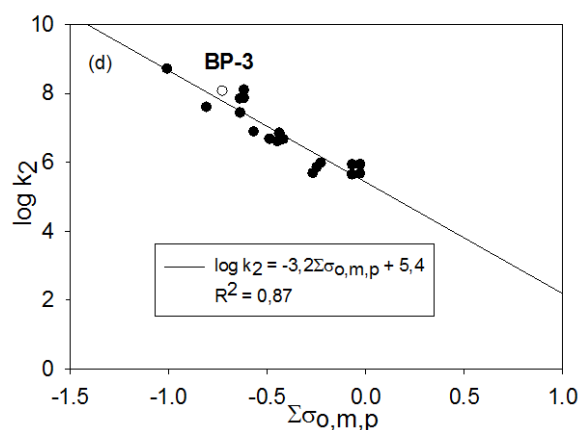
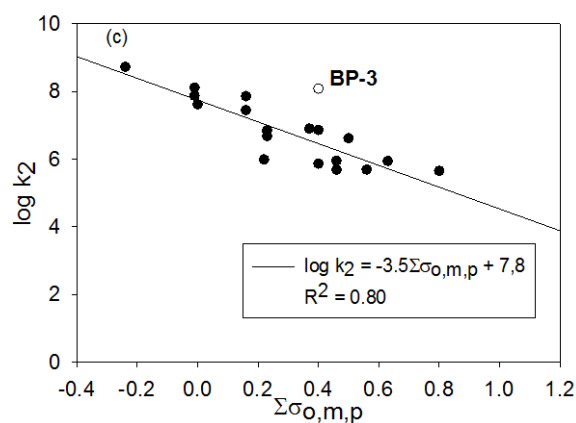
### Classical Hammett-type correlations

### Corrected Hammett-type correlations

#### Chlorination

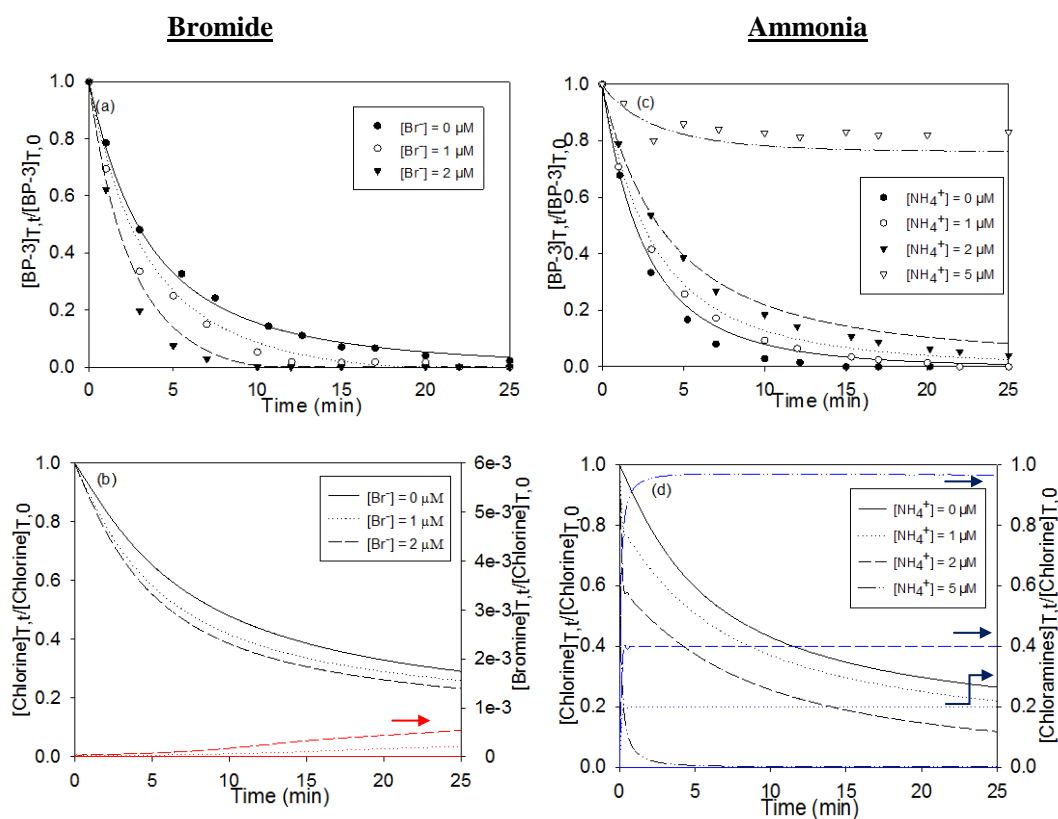


#### Bromination



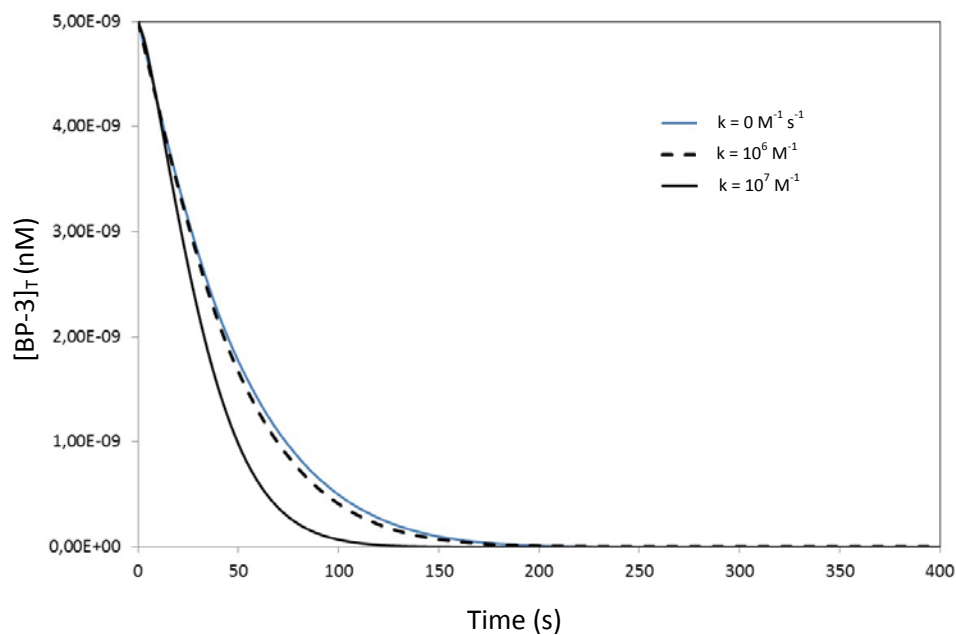
**Figure S4.** Cross-linear correlations between the second-order rate constants for the reactions of phenoxide ions with HOCl and HOBr and the Hammett constants  
(a) and (c) Classical Hammett-type correlations obtained from literature data <sup>(9,10)</sup>  
(b) Corrected Hammett-type correlation for phenol chlorination (obtained from data obtained for both monohydroxybenzenes and meta-dihydroxybenzenes) <sup>(12)</sup>  
(d) Corrected Hammett-type correlation obtained in this work for phenol bromination

## Chlorination in the presence of bromide and ammonia at pH 8.5



**Figure S5.** BP-3 chlorination in the presence of bromide or ammonia at pH 8,5  
 ( $[BP-3]_{T,0} = 1.4 (\pm 0.1) \mu M$ ,  $[Chlorine]_{T,0} = 5 (\pm 0.2) \mu M$  and  $T = 20 \pm 2^\circ C$ )  
 (a,b);  $[NH_4^+] = 0 \mu M$  and  $[Br^-] = 0-2 \mu M$  (c,d);  $[Br^-] = 0 \mu M$  and  $[NH_4^+] = 0-5 \mu M$   
 Symbols represent experimental data and solid lines represent the modeling obtained *via* Copasi

### Haloamines impact on BP-3 decay under drinking water treatment conditions



**Figure S6.** Estimation of haloamines contribution on BP-3 decay at pH =7,

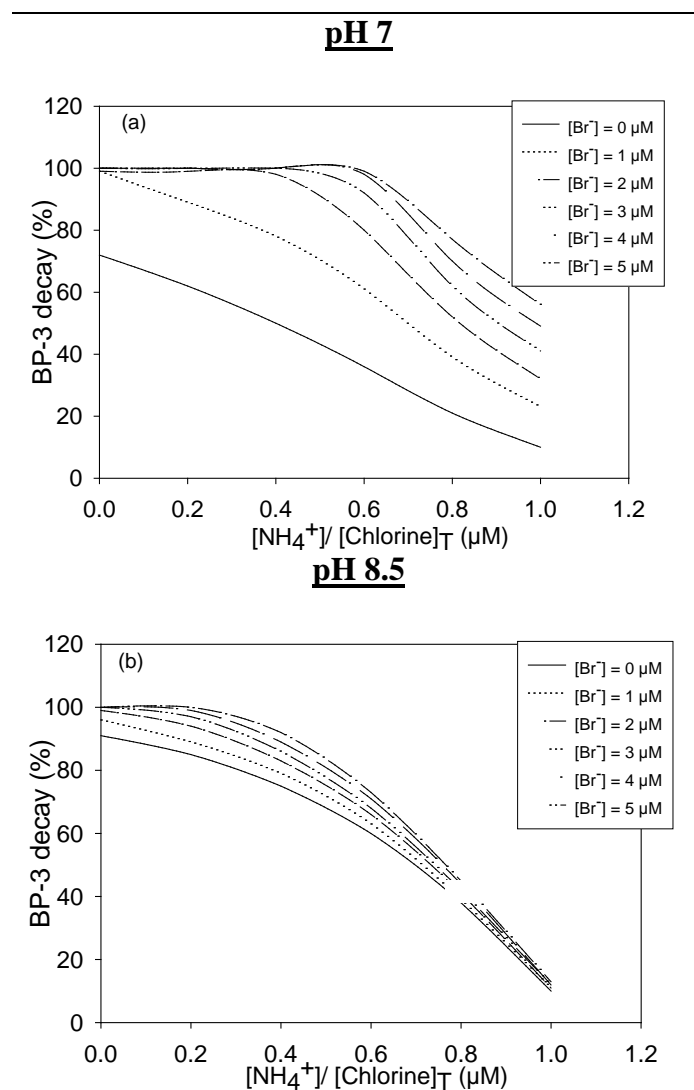
[Chlorine]<sub>T,0</sub> = 20 μM, [NH<sub>4</sub><sup>+</sup>] = [Br<sup>-</sup>] = 1 μM and [BP-3]<sub>T,0</sub> = 5 nM,

Luh and Marinas model was used to estimate haloamines formation<sup>(16)</sup>.

Rate constant obtained in this work was considered for monochloramine reaction with BP-3 and different elementary rate constants from 0 to 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> were tested for the reactions of other haloamine species



### **BP-3 decay during chlorination in the presence of bromide and ammonia**



**Figure S7.** (a,b) BP-3 decay patterns during chlorination in the presence of different bromide and ammonia concentrations ( $t = 10$  min,  $[\text{BP-3}]_{T,0} = 1.4 \mu\text{M}$ ,  $[\text{Chlorine}]_{T,0} = 5 \mu\text{M}$ )

## References

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